| | |
|---|---|
| **Test Material:** | Pymetrozine |
| **MRID:** | 49921303 |
| **Title:** | CGA 215944. Metabolism of $^{14}$C-Pyridine Ring Labelled CGA 215944 in Soil Under Aerobic Conditions at 20°C. Final Report. |
| **EPA PC Code:** | 101103 |
| **OCSPP Guideline:** | 835.4100 |

**For CDM/CSS-Dynamac JV**

**Primary Reviewer:** Kathleen Ferguson **Signature:** Kathleen P. Ferguson

**Date:** 11/10/16

**Secondary Reviewer:** Mary Samuel **Signature:** Mary Samuel

**Date:** 11/10/16

**QC/QA Manager:** Joan Gaidos **Signature:**

**Date:** 11/10/16

*This Data Evaluation Record may have been altered by the Environmental Fate and Effects Division subsequent to signing by CDM/CSS-Dynamac JV personnel.*

**Aerobic degradation of Pymetrozine in soil**

| | |
|---|---|
| Report: | MRID 49921303. Schulze-Aurich, J. 1996. CGA 215944. Metabolism of $^{14}$C-Pyridine Ring Labelled CGA 215944 in Soil Under Aerobic Conditions at 20°C. Final Report. Unpublished study performed by Ciba-Geigy Ltd., Basel, Switzerland; sponsored by Syngenta Ltd, Basel, Switzerland; and submitted by Syngenta Crop Protection, LLC, Greensboro, North Carolina. Report and Study No.: 94GJ01. Task No.: TK0290225. Experiment started July 4, 1994, and completed October 27, 1995 (p. 8). Final Report issued January 31, 1996. |
| Document No.: | MRID 49921303 |
| Guideline: | OCSPP 835.4100 |
| Statements: | The study was conducted in accordance with OECD and Swiss GLP standards (pp. 3, 5). Signed and dated Data Confidentiality, GLP, and Quality Assurance statements were provided (pp. 2-3, 5-6). A certification of the authenticity of the report was not included; an audit of the final report is listed in the Quality Assurance statement (p. 6). |
| Classification: | This study is classified SUPPLEMENTAL. The study author failed to use solvents with a range of dielectric constants (including a nonpolar solvent) to maximize extraction of the residues; unextracted residues totaled up to 42.22-65.95% of the applied. Length and conditions of storage of the soil prior to use, and of the extracted soil and soil extracts after sampling were not reported. |
| PC Code: | 101103 |
| Reviewer: | Jessica Joyce, MS, Fate Scientist<br>U.S. EPA |
| | Signature: Jessica Joyce Date: 2017.07.19 11:38:00 -04'00'<br>Date: July 19, 2017 |
| Secondary Reviewer: | Rochelle F. H. Bohaty, PhD, Senior Chemist<br>U.S. EPA |
| | Signature: Rochelle F H Bohaty<br>Date: July 19, 2017 |

**EXECUTIVE SUMMARY**

The aerobic transformation of [pyridinyl-5-$^{14}$C]pymetrozine (CGA 215944) was studied in a silt loam soil (Les Evouettes, pH 7.30) and a sandy loam soil (Collombey, pH 7.20) from Switzerland for up to 363 days in darkness at 20°C and a soil moisture content of 75% of field capacity. The soils were treated at 0.2989 mg a.i./kg, equivalent to a field application rate of 0.3 kg a.i./ha (0.268 lb a.i./A). Duplicate samples (duplicate flasks) of each silt loam soil and single samples (single flasks) of each sandy loam soil were collected at each sampling interval. It was not confirmed that aerobic conditions were maintained in the soils throughout the study. The soils were viable at study initiation and at termination.

Overall mass balances averaged 105.40 ± 2.27% of the applied (range 101.42-109.50%) in the silt loam soil and 97.77 ± 5.76% (range 91.38-111.05%) in the sandy loam soil. Except for a single sample of the sandy loam soil, recoveries were within guideline criteria (90-110%).

Observed $DT_{50}$ values, calculated half-lives, and information on transformation products are listed in **Table 1**. Pymetrozine dissipated with $t_{R\ IORE}$ values (IORE) of 20.2 days in the silt loam soil and 4.96 days in the sandy loam soil. Two major transformation products were isolated and two minor transformation products were identified.

In the silt loam soil, total extractable radioactivity declined from 107.67% of the applied at time 0 to 40.41% at 363 days, posttreatment. Unextracted radioactivity increased to a maximum of 42.22% of the applied at 272 days and was 41.86% at 363 days. In the 272-day sample, an additional 6.66% of the applied was extracted using refluxing with acetonitrile and acidified acetonitrile. Organic matter fractionation of the refluxed soil identified 7.69% of the applied was fulvic acids, 3.23% was humic acids, and 24.64% was humin. At study termination, $CO_2$ totaled a maximum of 22.48%. Organic volatiles were ≤0.01% throughout the experiment.

In the sandy loam soil, total extractable radioactivity declined from 108.95% of the applied at time 0 to 16.84% at 363 days posttreatment. Unextracted radioactivity increased to a maximum of 65.95% of the applied at 150 days and was 47.37% at 363 days. In the 272-day sample, an additional 5.10% of the applied was extracted using refluxing with acetonitrile and acidified acetonitrile. Organic matter fractionation of the refluxed soil identified 10.05% of the applied was fulvic acids, 6.79% was humic acids, and 22.44% was humin. At study termination, $CO_2$ totaled a maximum of 30.55%. Organic volatiles were ≤0.01% throughout the experiment.

**Table 1. Results Synopsis: Aerobic Soil Metabolism of Pymetrozine.**

| Soil Location and Texture (Temperature, pH) | Observed $DT_{50}$ (days) | Calculated Half-life[A] (days) | Model Parameters and Statistics | Transformation Products (maximum % AR, associated interval)[B] | |
|---|---|---|---|---|---|
| | | | | Major | Minor |
| Switzerland<br>Silt loam soil<br>(20°C, pH 7.30) | 3-7 | $t_{R\ IORE}$ = 20.2<br>IORE | $C_0$ = 103<br>N = 2.62<br>k = 0.000205<br>$S_C$ = 157<br>$S_{SFO}$ = 1.6e+03 | MB1 (55.01%, 14 days; $t_{R\ IORE}$ = 99.2 days)<br>MB5 (21.38%, 90 days; SFO DT50 = 382 days)<br>$CO_2$ (22.48%, 363 days)<br>Unextracted residues (42.22%, 272 days) | MB4 (9.43%, 150 days)<br>MB10 (2.47%, 363 days) |
| Switzerland<br>Sandy loam soil<br>(20°C, pH 7.20) | 1-3 | $t_{R\ IORE}$ = 4.96<br>IORE | $C_0$ = 95.5<br>N = 1.78<br>k = 0.0113<br>$S_C$ = 52.5<br>$S_{SFO}$ = 206 | MB1 (44.97%, 3 days; SFO DT50 = 27.3 days)<br>MB5 (22.93%, 30 days; SFO DT50 = 78.7 days)<br>$CO_2$ (30.55%, 363 days)<br>Unextracted residues (65.95%, 150 days) | MB4 (7.14%, 59 days)<br>MB10 (2.59%, 90 days) |

[A] Calculated half-lives, model parameters, and kinetics models in accordance with the NAFTA kinetics guidance (USEPA, 2012); Indeterminate Order Rate Equation (IORE), Single First-Order (SFO).
[B] AR means "applied radioactivity".
MB 1 = CGA 359009; 4,5-Dihydro-5-hydroxy-6-methyl-4-[(3-pyridinylmethylene)amino]-1,2,4-triazine-3-(2H)-one.
MB4 = CGA 363430; 6-Methyl-4-[(6-oxo-l,6-dihydro-pyridine-3-ylmethylene)-ammo]-2H-[l,2,4]triazine-3,5-dione.
MB5 = CGA 366431; 5-Hydroxy-6-methyl-4-[(6-oxo-l,6-dihydro-pyridine-3-ylmethylene)-amino]-4,5-dihydro-2H-[l,2,4]triazine-3-one.
MB10 = CGA 300407; 3-Pyridinecarboxaldehyde.

Page numbers cited in this DER refer to the numbers in the lower right hand corner of each page.

## I. Materials And Methods

### A. Materials:

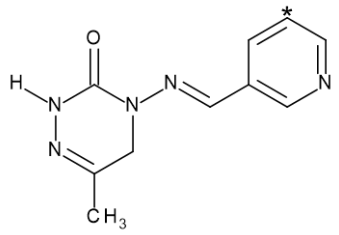
**1. Test Material** [Pyridinyl-5-$^{14}$C]pymetrozine (CGA 215944; p. 18)

Specific activity: 2.12 MBq/mg

Radiochemical purity: 98.7% (p. 31)

Chemical purity: Not reported

Batch Number: Ko-10.2A (p. 18)



Solubility in water (20˚C) 270 mg/L at 20°C (p. 17)

**2. Reference Compounds:** The following standards were used in the analysis (**Table 2**).

**Table 2. Reference Compounds.**

| Applicant's Code Name | Chemical Name | Purity (%) | Batch No. |
|---|---|---|---|
| Pymetrozine (CGA 215944) | (E)-4,5-Dihydro-6-methyl-4-(3-pyridylmethyleneamino)-1,2,4-triazin-3(2H)-one | 99.7 | AMS 522/102 |
| CGA 300407 | 3-Pyridinecarboxaldehyde | 93 ± 2 | RV-2371 |
| CGA 129539 | 2-(Pyridine-3-carbonylamino)acetic acid | 98 | N-4751 |
| CGA 180778 | Pyridine-3-carboxamide | 100 | F 72340 |
| CGA 180777 | Nicotinic acid | 99 | 72309 |
| CGA 128632 | 3-Pyridylmethanol | 97 | 55780 |
| CGA 79452 | Pyridine-3-carbohydrazide | -- | AM 2075 |
| CGA 323584 | 6-Methyl-4-[(E)-3-pyridylmethyleneamino]-2H-1,2,4-triazine-3,5-dione | 93 ± 2 | RV-2437/2 |
| CGA 320484 | 4-[(E)-3-Pyridylmethyleneamino]-2,5-dihydro-1,2,4-triazin-3-one | 97 | HK-9071/2R |
| CGA 319251 | 6-Hydroxypyridine-3-carboxylic acid | 99 | RV-2442/1 |
| CGA 313124 | 6-(Hydroxymethyl)-4-[(E)-3-pyridylmethyleneamino]-2,5-dihydro-1,2,4-triazin-3-one | 99 | HK-8903/3R |
| CGA 245342 | 6-Methyl-4-[(E)-(1-oxidopyridin-1-ium-3-yl)methyleneamino]-2,5-dihydro-1,2,4-triazin-3-one | 89.9 | OK-7926 |
| CGA 96956 | 1-Methylpyridin-1-ium-3-carboxylate | -- | 5411.1 |
| Reference 2U (CGA 359009) | 4,5-Dihydro-5-hydroxy-6-methyl-4-[(3-pyridinylmethylene)amino]-1,2,4-triazine-3-(2H)-one | -- | DAH-XX-32 |

Data obtained from Table 1, pp. 38-39, of the study report, and DER Attachment 1.
-- = not reported.

**3. Soil:** Soil collection and characterization are summarized in **Table 3** and **Table 4**, respectively.

**Table 3. Description of Soil Collection and Storage.**

| Description | Les Evouettes | Collombey |
|---|---|---|
| Geographic location | Les Evouettes/VS, Switzerland | Collombey/VS, Switzerland |
| Site Description | Not reported | |
| Soil series | Not provided | |
| Pesticide use history at the collection site | Not reported | |
| Collection date | Not reported | |
| Collection procedures | Not reported | |
| Sampling depth | Not reported | |
| Storage conditions | Not reported | |
| Storage length | Not reported | |
| Soil preparation | Sieved to 2 mm | |

Data obtained from pp. 18-19 of the study report.

**Table 4. Properties of the Soil.**

| Property | Les Evouettes | Collombey |
|---|---|---|
| Soil Texture (USDA) | Silt loam | Sandy loam |
| % Sand | 31.80 | 64.50 |
| % Silt | 54.30 | 23.70 |
| % Clay | 13.90 | 11.80 |
| pH | 7.30 | 7.20 |
| Organic carbon (%) | 2.10 | 1.70 |
| Organic matter (%)[1] | 3.62 | 2.93 |
| Cation Exchange Capacity (mmol/Z/100 g) | 14.00 | 11.90 |
| $CaCO_3$ equivalence (%) | 8.50 | 4.50 |
| Soil Moisture Content (g/100 g soil) | | |
| MWHC | 58.25 | 50.03 |
| Field Capacity | 47.43 | 32.23 |
| Bulk density ($g/cm^3$) | Not reported | |
| Microbial Population (mg C/100 g) | | |
| Day 0 | 58.55 | 61.97 |
| Day 182 | 47.50 | 43.30 |
| Day 359 | 40.77 | 33.83 |
| Soil taxonomic classification | Not reported | |

Data obtained from Table 2, p. 40, in the study report. The soil texture was confirmed using USDA-NRCS technical support tools.

1 Calculated by the reviewer as: organic matter (%) = organic carbon (%) x 1.724.

## B. STUDY DESIGN

### 1. Experimental Conditions: (Summarized in **Table 5**).

**Table 5. Experimental Design.**

| Property | Details |
|---|---|
| Duration of the test (days) | 363 days |
| Soil condition (Air dried/fresh) | Not reported. |
| Soil (g/replicate) | 200 g (dry wt) |
| Application rates | |
| Nominal | 0.3 mg/kg, equivalent to a field rate of 0.3 kg a.i./ha (0.268 lb a.i./ A) |
| Actual | 29.89 µg/100 g |
| Control conditions (if used) | No sterile controls were used. |
| Number of Replicates | |
| Controls (if used) | No sterile controls were used. |
| Treatment | Duplicate flasks of each silt loam soil and single flasks of each sandy loam soil were collected at each sampling interval. |
| Test apparatus | |
| Type/material/volume | Glass flasks (not described) containing moist soil were attached to flow-through volatile trapping systems and incubated in darkness in a temperature-controlled environmental chamber. The test apparatus is illustrated in Figure 2, p. 50. |
| Details of traps for $CO_2$ and other volatiles (if any) | Humidified air was drawn through sample (60 mL/minute), then through one bottle of 0.25N $H_2SO_4$ and two bottles of 2N NaOH. The volatile trapping system is illustrated in Figure 2, p. 50. |
| If no traps were used, is the system closed/open? | Volatile traps were used. |
| Identity and concentration of co-solvent | Acetone; *ca*. 0.2% acetone by volume (760 µL of a 40% acetone solution/200 g soil) |
| Test Material: | |
| Volume of the test solution used/treatment | 760 µL /200 g |
| Application method | Applied to the soil surface using a Hamilton syringe; the soils were then mixed by shaking the flasks. |
| Is the co-solvent evaporated? | No |
| Any indication of the test material adsorbing to the walls of the test apparatus? | None |
| Experimental conditions: | |
| Temperature (°C) | 20 ± 0.7°C |
| Continuous darkness | Yes |
| Moisture content | 75% of field capacity |
| Moisture maintenance method | Adjusted weekly during the first month and at *ca.* 2-week intervals thereafter. |
| Other details (if any) | None |

Data obtained from pp. 19-21; Table 3, p. 41; and Figure 2, p. 50, of the study report.

**2. Sampling During Study Period:** (Details summarized in **Table 6**).

**Table 6. Sampling During Study Period.**

| Criteria | Details |
|---|---|
| Sampling intervals (days) | 0, 1, 3, 7, 14, 30, 59, 90, 150, 272, and 363 days. |
| Sampling method | Duplicate flasks of each silt loam soil and single flasks of each sandy loam soil were collected at each sampling interval. |
| Method of collection of $CO_2$ and organic volatile compounds | Volatile traps were collected at each interval. |
| Sampling intervals/times for: | |
| Sterility check (if used) | Sterile samples were not used. |
| Moisture content | Soil moisture was adjusted weekly during the first month and at *ca.* 2-week intervals thereafter. |
| Redox potential, other | The redox potential was not measured. |
| Sample storage before analysis | Sample storage was not described. It was not reported whether the soils were stored prior to extraction or the soil extracts were stored prior to analysis. |
| Other observation (if any) | None. |

Data obtained from pp. 23-24; and Tables 3-5, pp. 41-43, of the study report.

**3. Analytical Procedures:**

**Extraction Methods:** The soil was extracted four times with acetonitrile:water (80:20, v:v) and once with water by shaking (20 minutes/extraction) at room temperature ("cold extracts"; p. 21). After each extraction, the samples were centrifuged and the supernatant decanted and filtered. Aliquots were analyzed using LSC. The extracts were combined, concentrated under reduced pressure, and centrifuged. Aliquots of the supernatants were analyzed using HPLC (pp. 21, 23).

The soil was then Soxhlet-extracted with acetonitrile for 8 hours, and the extract and soil were separated by centrifuging (p. 21). Aliquots were analyzed using LSC, and extracts containing more than 1% of the applied were concentrated and combined with the cold extracts prior to HPLC analysis.

Select samples (150 and 272 days for silt loam, 90 and 272 days for sandy loam) were then extracted by refluxing (80°C) with acetonitrile:water (4:1, v:v) for 2 hours, then with acetonitrile:0.1N HCl (9:1, v:v) for 2 hours ("harsh extractions"; pp. 21-22; Table 6, p. 44). After each extraction, the samples were centrifuged and the solvent decanted. Aliquots were concentrated and analyzed using HPLC.

**Determination of Unextracted Residues:** Portions of the extracted soils were air-dried, homogenized, and analyzed for total remaining radioactivity using LSC following combustion (p. 22).

The soil extracted by refluxing (harsh extraction) was further extracted with 0.5N NaOH for *ca*. 17 hours by shaking at room temperature (p. 22; Table 7, p. 45). The supernatant was acidified to ≤pH 1, and the resulting supernatant (fulvic acids) and precipitate (humic acids) were quantified using LSC. The concentration of humin was determined by subtraction (p. 23).

**Determination of Volatile Compounds:** Aliquots of the trapping solutions were analyzed quantified using LSC (p. 23). The identification of residues as $CO_2$ in the trapping solutions was confirmed by reacting the NaOH solution with $H_2SO_4$.

**Total radioactivity measurement:** Total [$^{14}$C]residues were determined by summing the concentrations of residues in the soil extracts, extracted soil, and volatile traps (Tables 4-5, pp. 42-43).

**Derivatization method** A derivatization method was not employed.

**Identification and quantification of Parent and Transformation Compounds:** Aliquots of the soil extracts were analyzed by HPLC using a Nucleosil C-18 column eluted with a gradient mobile phase of (A) water and (B) acetonitrile with UV and radioactive flow detection (pp. 24-26). HPLC peaks were identified by comparison to reference standards that were cochromatographed with the samples (p. 27).

To confirm the results of the HPLC analyses, aliquots of the extracts were analyzed by two-dimensional TLC on silica gel plates developed in ethyl acetate:methanol:water (60:30:5, v:v:v) and chloroform:methanol:water (60:30:5, v:v:v; p. 28). Radioactive regions were located and quantified using autoradiography; reference standard were located using UV light.

Samples were also analyzed using high voltage electrophoresis (p. 29).

The identity of isolated compounds was confirmed using mass spectroscopy and NMR spectroscopy (p. 29).

**Detection Limits (LOD, LOQ) for the Parent and Transformation Products:** For HPLC, the Limit of Detection (LOD) was 0.0003 ppm and the Limit of Quantification (LOQ) was 0.0005 (Appendix B, p. 74). For LSC, background was 0.00000012-0.00000029 mg; LOD and LOQ were not reported.

## II. Results and Discussion

### A. Data

Study results including total mass balances and distribution of radioactivity are presented in **Tables 7a-7b**. No determinations were made to verify that aerobic conditions were maintained in the soils. Soils were viable at study initiation and termination (p. 31; Table 2, p. 40).

### B. Mass Balance

Overall mass balances averaged 105.40 ± 2.27% of the applied (range 101.42-109.50%) in the silt loam soil and 97.77 ± 5.76% (range 91.38-111.05%) in the sandy loam soil (Tables 4-5, pp. 42-43). Except for a single sample of the sandy loam soil, recoveries were within guideline criteria (90-110%).

## C. Unextracted and Extractable Residues

In the silt loam soil, total extractable radioactivity declined from 107.67% of the applied at time 0 to 40.41% at 363 days posttreatment (Table 4, p. 42). Unextracted radioactivity increased to a maximum of 42.22% of the applied at 272 days and was 41.86% at 363 days. In the 272-day sample, an additional 6.66% of the applied was extracted using refluxing with acetonitrile and acidified acetonitrile (Table 6, p. 44). Organic matter fractionation of the refluxed soil (35.56% unextracted) identified 7.69% of the applied was fulvic acids, 3.23% was humic acids, and 24.64% was humin (Table 7, p. 45).

In the sandy loam soil, total extractable radioactivity declined from 108.95% of the applied at time 0 to 16.84% at 363 days posttreatment (Table 5, p. 43). Unextracted radioactivity increased to a maximum of 65.95% of the applied at 150 days and was 47.37% at 363 days. In the 272-day sample, an additional 5.10% of the applied was extracted using refluxing with acetonitrile and acidified acetonitrile (Table 6, p. 44). Organic matter fractionation of the refluxed soil (39.28% unextracted) identified 10.05% of the applied was fulvic acids, 6.79% was humic acids, and 22.44% was humin (Table 7, p. 45).

## D. Volatilization

At study termination, $CO_2$ totaled maximums of 22.48% and 30.55% of the applied in the silt loam and sandy loam soils, respectively (Tables 4-5, pp. 42-43). Organic volatiles were ≤0.01% of the applied in the two soils throughout the experiments.

**Table 7a. Aerobic transformation of [pyridinyl-5-$^{14}$C]Pymetrozine, expressed as a percentage of the applied radioactivity, in silt loam soil.**

| Sampling Interval (days) | 0 | | 1 | | 3 | | 7 | | 14 | | 30 | | 59 | | 90 | | 150 | | 272 | | 363 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Replicate Number | A | B | A | B | A | B | A | B | A | B | A | B | A | B | A | B | A | B | A | B | A | B |
| Pymetrozine (CGA 215944) | 102.82 | 102.57 | 77.28 | 77.97 | 53.86 | 51.29 | 41.94 | 40.91 | 20.65 | 21.55 | 16.64 | 15.02 | 8.52 | 10.87 | 10.27 | 14.02 | 7.96 | 6.89 | 5.41 | 4.85 | 3.11 | 2.94 |
| MB1 | 4.85 | 5.17 | 18.54 | 18.27 | 31.96 | 35.19 | 40.06 | 40.54 | 55.01 | 52.33 | 45.71 | 46.82 | 30.61 | 32.77 | 26.06 | 29.09 | 18.67 | 17.43 | 6.81 | 6.17 | 6.43 | 5.81 |
| MB4 | 0.00 | 0.00 | 0.00 | 0.00 | 1.22 | 1.26 | 1.60 | 1.96 | 2.10 | 2.28 | 4.55 | 4.11 | 4.64 | 6.69 | 7.17 | 5.33 | 8.14 | 9.43 | 8.07 | 8.68 | 8.36 | 7.99 |
| MB5 | 0.00 | 0.00 | 0.00 | 0.00 | 3.10 | 3.88 | 5.08 | 4.85 | 9.87 | 7.95 | 14.62 | 16.07 | 18.07 | 18.81 | 21.38 | 18.43 | 19.28 | 18.79 | 14.01 | 13.65 | 12.93 | 12.49 |
| MB10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.41 | 1.55 | 2.23 | 1.74 | 1.74 | 2.47 |
| Others[1] | 0.00 | 0.00 | 1.66 | 1.96 | 3.94 | 5.33 | 5.55 | 5.03 | 3.75 | 7.22 | 5.96 | 5.33 | 6.34 | 4.26 | 4.07 | 3.29 | 5.75 | 8.00 | 7.12 | 7.44 | 7.84 | 8.10 |
| Extractable residues | 107.67 | 107.74 | 97.48 | 98.20 | 94.09 | 96.96 | 94.23 | 93.29 | 91.38 | 91.32 | 87.48 | 87.35 | 68.18 | 73.39 | 68.95 | 70.16 | 61.22 | 62.09 | 43.64 | 42.54 | 40.41 | 39.82 |
| Unextracted residues | 1.83 | 1.65 | 5.09 | 5.52 | 9.60 | 7.14 | 10.59 | 12.01 | 13.17 | 13.00 | 15.81 | 16.75 | 32.31 | 29.51 | 31.52 | 31.83 | 34.03 | 31.25 | 39.64 | 42.22 | 41.86 | 41.50 |
| $CO_2$ | 0.00 | 0.00 | 0.09 | 0.09 | 0.19 | 0.22 | 0.48 | 0.46 | 1.08 | 1.05 | 2.32 | 2.50 | 4.75 | 5.20 | 7.57 | 6.89 | 10.32 | 10.13 | 18.13 | 17.60 | 21.85 | 22.48 |
| Volatile organics | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |
| Mass balance | 109.50 | 109.39 | 102.65 | 103.81 | 103.87 | 104.32 | 105.30 | 105.76 | 105.63 | 105.37 | 105.61 | 106.60 | 105.24 | 108.11 | 108.06 | 108.89 | 105.57 | 103.46 | 101.42 | 102.35 | 104.12 | 103.80 |

Data obtained from Table 4, p. 42, and Table 9, p. 46, of the study report.

1 Others is the sum of minor HPLC peaks MB2, MB7, MB8, MB9, MB11 and MB12.

MB 1 = CGA 359009; 4,5-Dihydro-5-hydroxy-6-methyl-4-[(3-pyridinylmethylene)amino]-1,2,4-triazine-3-(2H)-one.

MB4 = CGA 363430; 6-Methyl-4-[(6-oxo-l,6-dihydro-pyridine-3-ylmethylene)-ammo]-2H-[l,2,4]triazine-3,5-dione.

MB5 = CGA 366431; 5-Hydroxy-6-methyl-4-[(6-oxo-l,6-dihydro-pyridine-3-ylmethylene)-amino]-4,5-dihydro-2H-[l,2,4]triazine-3-one.

MB10 = CGA 300407; 3-Pyridinecarboxaldehyde.

**Table 7b. Aerobic transformation of [pyridinyl-5-$^{14}$C]Pymetrozine, expressed as a percentage of the applied radioactivity, in sandy loam soil.**

| Sampling Interval (days) | 0 | 1 | 3 | 7 | 14 | 30 | 59 | 90 | 150 | 272 | 363 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Replicate Number** | **A** | **A** | **A** | **A** | **A** | **A** | **A** | **A** | **A** | **A** | **A** |
| Pymetrozine (CGA 215944) | 94.68 | 70.95 | 37.51 | 24.81 | 10.78 | 4.55 | 2.40 | 0.00 | 0.00 | 1.62 | 1.03 |
| MB1 | 11.88 | 20.98 | 44.97 | 39.26 | 40.14 | 24.30 | 8.90 | 3.15 | 1.58 | 1.75 | 1.57 |
| MB4 | 0.00 | 0.00 | 1.68 | 1.74 | 0.00 | 6.29 | 7.14 | 4.45 | 3.61 | 4.95 | 3.03 |
| MB5 | 0.00 | 0.00 | 4.85 | 12.27 | 14.72 | 22.93 | 19.89 | 10.29 | 6.49 | 6.08 | 2.54 |
| MB10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.40 | 2.59 | 1.94 | 2.53 | 1.99 |
| Others[1] | 2.40 | 2.16 | 4.39 | 8.88 | 8.77 | 4.24 | 4.52 | 5.14 | 4.16 | 4.71 | 6.68 |
| Extractable residues | 108.95 | 94.10 | 93.39 | 86.96 | 74.41 | 62.32 | 45.24 | 25.63 | 17.77 | 21.65 | 16.84 |
| Unextracted residues | 2.10 | 3.32 | 9.00 | 6.59 | 17.36 | 23.97 | 39.77 | 60.53 | 65.95 | 44.38 | 47.37 |
| $CO_2$ | 0.00 | 0.09 | 0.22 | 0.17 | 2.27 | 5.10 | 11.09 | 13.01 | 18.64 | 26.68 | 30.55 |
| Volatile organics | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| Mass balance | 111.05 | 97.51 | 102.61 | 93.72 | 94.04 | 91.38 | 96.11 | 99.17 | 102.37 | 92.72 | 94.76 |

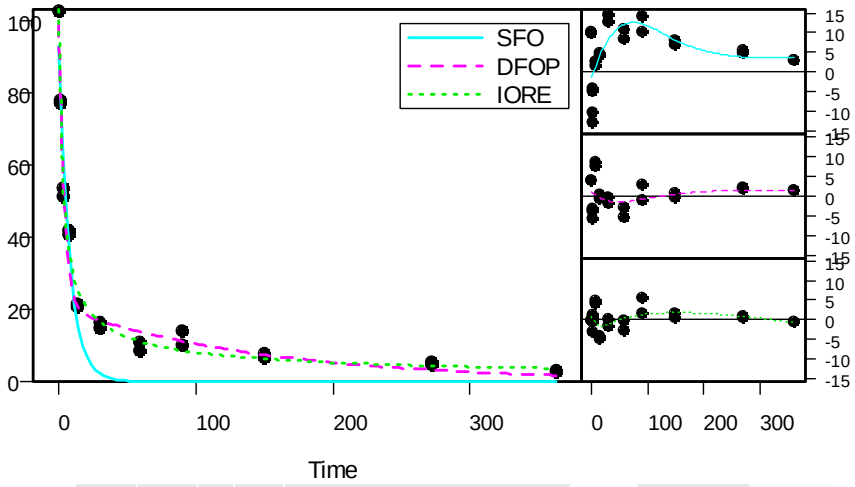
Data obtained from Table 5, p. 43, and Table 9, p. 47, of the study report.
1 Others is the sum of minor HPLC peaks MB2, MB7, MB8, MB9, MB11 and MB12.
MB 1 = CGA 359009; 4,5-Dihydro-5-hydroxy-6-methyl-4-[(3-pyridinylmethylene)amino]-1,2,4-triazine-3-(2H)-one.
MB4 = CGA 363430; 6-Methyl-4-[(6-oxo-l,6-dihydro-pyridine-3-ylmethylene)-ammo]-2H-[l,2,4]triazine-3,5-dione.
MB5 = CGA 366431; 5-Hydroxy-6-methyl-4-[(6-oxo-l,6-dihydro-pyridine-3-ylmethylene)-amino]-4,5-dihydro-2H-[l,2,4]triazine-3-one.
MB10 = CGA 300407; 3-Pyridinecarboxaldehyde.

**E. Transformation of the Test Compound:** Transformation kinetics of the parent compound in the total system are summarized in the following **Figures**, with transformation product information summarized in **Table 8**. Transformation kinetics of MB1 and MB5 are summarized in DER Attachment 2.

Using a two-compartment model (MicroCal Origin 3.5), the study author determined pymetrozine DT50 values of 4 days in the silt loam soil and 2 days in the sandy loam soil (pp. 30, 32-33; Table 10, p. 48). In the silt loam soil, the DT50 was 74 days for MB1 and 389 days for MB5. In the sandy loam soil, the DT50 was 21 days for MB1, 335 days for MB4, and 78 days for MB5.

## Pymetrozine in aerobic silt loam soil

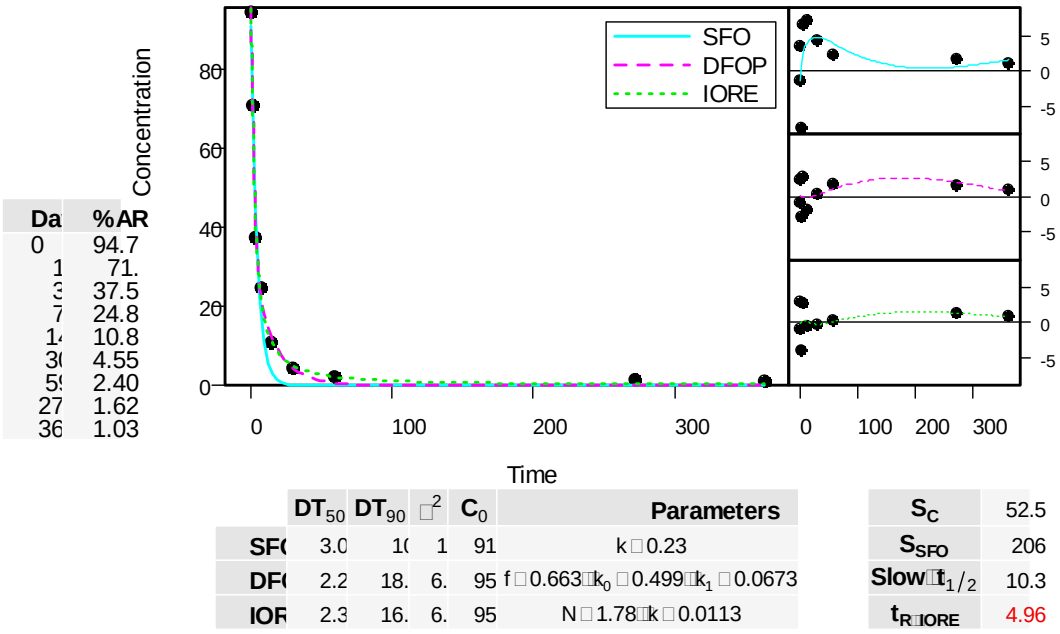
| Da | %AR |
|---|---|
| 0 | 103 |
| 1 | 77.3 |
| 3 | 53.9 |
| 7 | 41.9 |
| 14 | 20.6 |
| 30 | 16.6 |
| 59 | 8.52 |
| 90 | 10.3 |
| 15 | 7.96 |
| 27 | 5.41 |
| 36 | 3.11 |
| 0 | 103. |
| 1 | 78. |
| 3 | 51.3 |
| 7 | 40.9 |
| 14 | 21.6 |
| 30 | 15.0 |
| 59 | 10.9 |
| 90 | 14.0 |
| 15 | 6.89 |
| 27 | 4.85 |
| 36 | 2.94 |




| | $DT_{50}$ | $DT_{90}$ | $\chi^2$ | $C_0$ | Parameters |
|---|---|---|---|---|---|
| SF( | 5.6 | 18. | 2 | 92 | k 0.123 |
| DF( | 3.9 | 10 | 1 | 98 | f 0.79 $k_0$ 0.25 $k_1$ 0.00683 |
| IOF | 3.4 | 67. | 6. | 1( | N 2.62 k 0.000205 |

| | |
|---|---|
| $S_C$ | 157 |
| $S_{SFO}$ | 1.6e+03 |
| Slow $t_{1/2}$ | 101 |
| $t_{R\ IORE}$ | 20.2 |

# Pymetrozine in aerobic sandy loam soil




| Da | %AR |
|---|---|
| 0 | 94.7 |
| 1 | 71. |
| 3 | 37.5 |
| 7 | 24.8 |
| 14 | 10.8 |
| 30 | 4.55 |
| 59 | 2.40 |
| 27 | 1.62 |
| 36 | 1.03 |

| | $DT_{50}$ | $DT_{90}$ | $\chi^2$ | $C_0$ | Parameters |
|---|---|---|---|---|---|
| SFO | 3.0 | 10 | 1 | 91 | k 0.23 |
| DFO | 2.2 | 18. | 6. | 95 | f 0.663 $k_0$ 0.499 $k_1$ 0.0673 |
| IOR | 2.3 | 16. | 6. | 95 | N 1.78 k 0.0113 |

| | |
|---|---|
| $S_C$ | 52.5 |
| $S_{SFO}$ | 206 |
| Slow $t_{1/2}$ | 10.3 |
| $t_{R\ IORE}$ | 4.96 |

Kinetics models: Single First Order (SFO); Double First Order in Parallel (DFOP), and Indeterminate Order Rate Equation (IORE). Calculated half-lives and model parameters in accordance with the NAFTA kinetics guidance (USEPA, 2012).

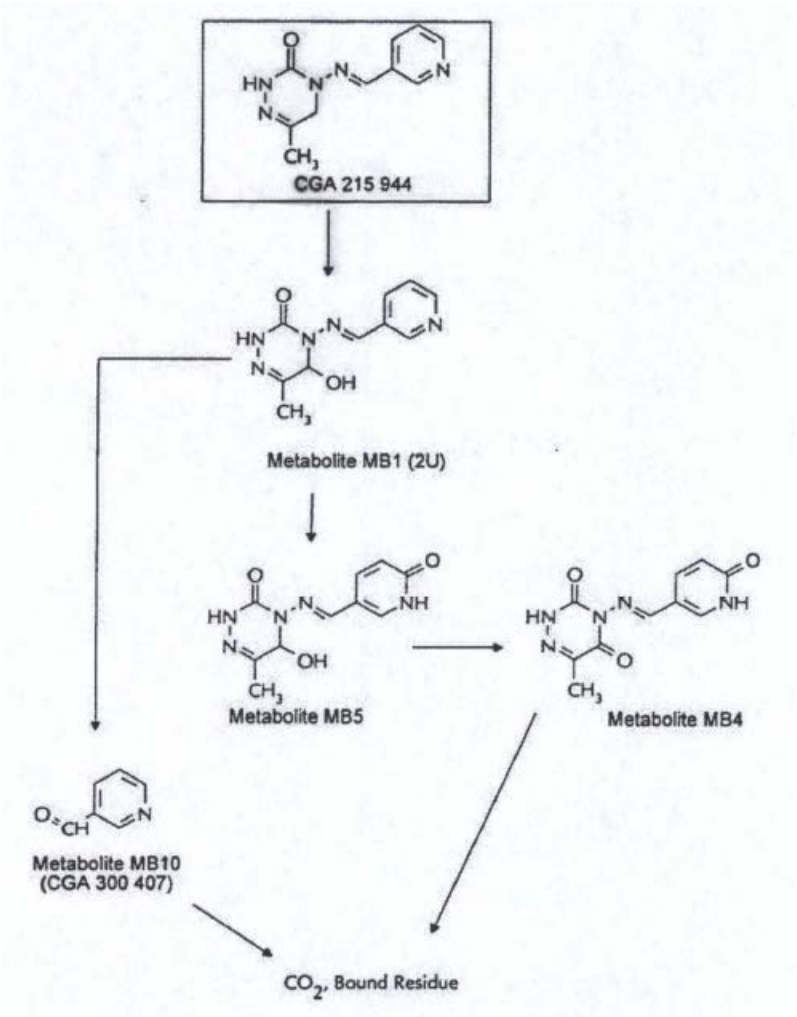
Observed nonvolatile transformation products are described in **Table 8**. No major transformation products were isolated, and no minor transformation products were identified.

**Table 8. Transformation Products of Pymetrozine in Soil.**

| | Transformation Products | Maximum %AR Observed | Associated Interval (days) | Final %AR Observed | Final Interval (days) |
|---|---|---|---|---|---|
| Switzerland Silt loam soil (20°C, pH 7.30) | MB1 | 55.01 | 14 | 6.43 | 363 |
| | MB4 | 9.43 | 150 | 8.36 | 363 |
| | MB5 | 21.38 | 90 | 12.93 | 363 |
| | MB10 | 2.47 | 363 | 2.47 | 363 |
| Switzerland Sandy loam soil (20°C, pH 7.20) | MB1 | 44.97 | 3 | 1.57 | 363 |
| | MB4 | 7.14 | 59 | 3.03 | 363 |
| | MB5 | 22.93 | 30 | 2.54 | 363 |
| | MB10 | 2.59 | 90 | 1.99 | 363 |

Data obtained from Tables 8-9, pp. 46-47, in the study report.
MB 1 = CGA 359009; 4,5-Dihydro-5-hydroxy-6-methyl-4-[(3-pyridinylmethylene)amino]-1,2,4-triazine-3-(2H)-one.
MB4 = CGA 363430; 6-Methyl-4-[(6-oxo-l,6-dihydro-pyridine-3-ylmethylene)-ammo]-2H-[l,2,4]triazine-3,5-dione.
MB5 = CGA 366431; 5-Hydroxy-6-methyl-4-[(6-oxo-l,6-dihydro-pyridine-3-ylmethylene)-amino]-4,5-dihydro-2H-[l,2,4]triazine-3-one.
MB10 = CGA 300407; 3-Pyridinecarboxaldehyde.

An aerobic transformation pathway in soil was provided by the study author (Figure 16, p. 66).




## III. STUDY DEFICIENCIES AND REVIEWER'S COMMENTS

1. Significant levels (42.22-65.95% of the applied) of unextracted residues were detected (Tables 4-5, pp. 42-43). The study author failed to use solvents with a range of dielectric constants (including a nonpolar solvent) to maximize extraction of the residues.

2. Refluxing the soil ("harsh extraction") at 90/150 and 272 days released an additional 5.10-8.96% of the applied radioactivity (Table 6, p. 44). The study author stated that the radioactive fractions detected in the harsh extracts by HPLC were identical to those observed in the Soxhlet extracts, but did not provide any quantitative data (p. 33; Figure 12, p. 62). The HPLC chromatogram provided (sandy loam soil, 90 days, 8.96% of the applied) indicated small amounts of parent, and transformation products MB1, MB4, MB5, MB7, MB9, and MB10.

3. It was not stated if the soil was stored prior to extraction. Length and conditions of storage of the soil extract prior to analysis were not reported. Storage of samples when not in use was not described. However, it was stated that the test substance proved to be stable during the time of

application shown in an earlier study (Valero, J. Gonzalez. Adsorption/Desorption of CGA 215944 with various soils. Crop Protection Division/Product Safety/Ecochemistry. Project Report Number PR 3/93, June 15, 1993.)

4. Soil collection dates and procedures were not reported. Length and conditions of storage of the soils prior to use in the study were not reported. The pesticide use history at the soil collection sites was not reported, and it was not demonstrated that the soils were free of pesticides prior to use.

5. The concentration of humin was determined by subtraction (p. 22). For accuracy, it is preferable if the concentration is determined by combustion of the NaOH-extracted soil.

6. Analysis of the sandy loam soil was not analyzed in duplicate.

7. Both the non-radiolabelled test substance, and radiolabelled test substance expired prior to the conclusion of testing.

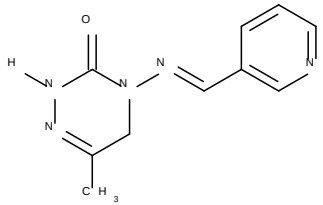
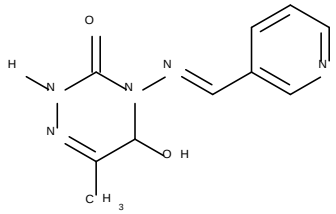
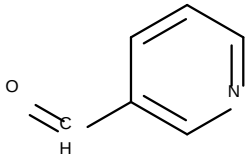
8. Half-life data may suggest that pymetrozine is more tightly bound to the silt loam soils ($t_{R\ IORE}$ = 20.2) compared to the sandy loam soil ($t_{R\ IORE}$ = 4.96) due to soil properties such as: surface area, cation exchange capacity, percent clay, and percent organic matter.

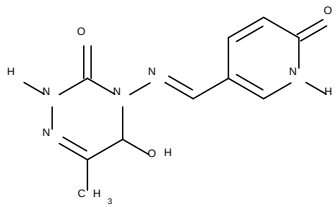
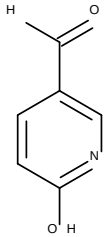
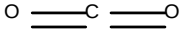
## IV. REFERENCES

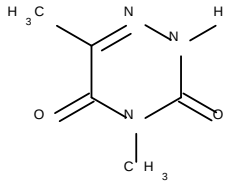
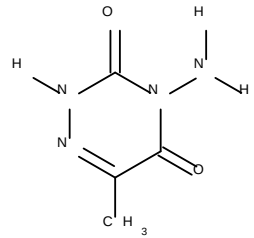
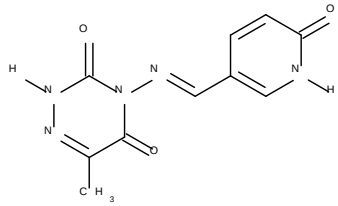
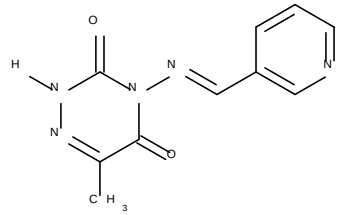
1. U.S. Environmental Protection Agency. 2008. Fate, Transport and Transformation Test Guidelines, OCSPP 835.4100, Aerobic Soil Metabolism. Office of Chemical Safety and Pollution Prevention, Washington, DC. EPA 712-C-08-016.

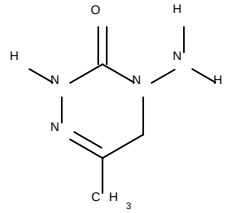
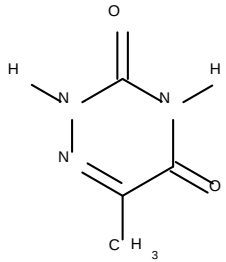
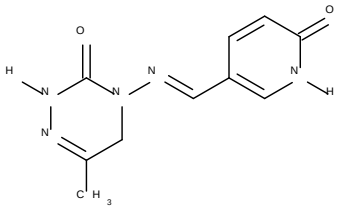
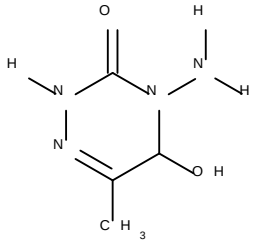
2. U.S. Environmental Protection Agency. 2012. NAFTA Guidance for Evaluating and Calculating Degradation Kinetics in Environmental Media.

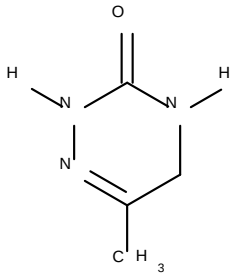
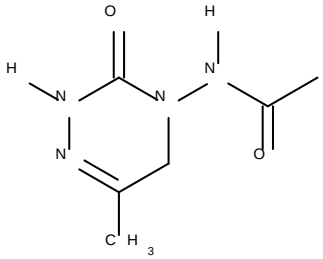
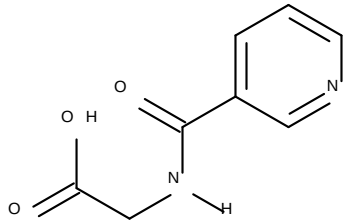
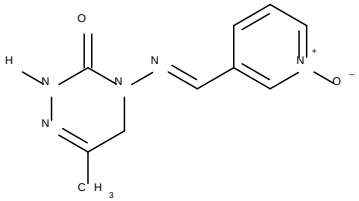
**DER ATTACHMENT 1. Pymetrozine and Its Environmental Transformation Products.** [A]

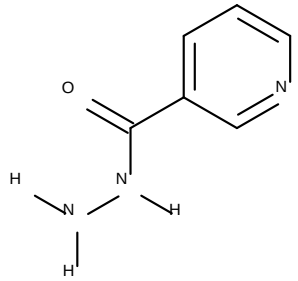
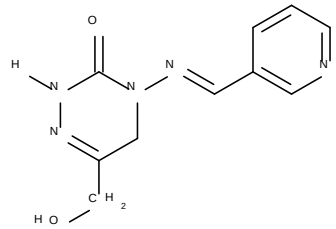
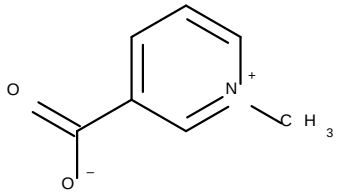
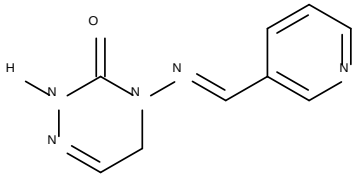
| Code Name/ Synonym | Chemical Name | Chemical Structure | Study Type | MRID | Maximum %AR (day) | | Final %AR (study length) |
|---|---|---|---|---|---|---|---|
| **PARENT** | | | | | | | |
| **Pymetrozine (CGA 215944, CSAA202913)** | **IUPAC:** (E)-4,5-dihydro-6-methyl-4-(3-pyridylmethyleneamino)-1,2,4-triazin-3(2H)-one<br><br>**CAS:** 4,5-Dihydro-6-methyl-4-[(E)-(3-pyridinylmethylene)amino]-1,2,4-triazin-3(2H)-one<br><br>**CAS No.:** 123312-89-0<br><br>**Formula:** $C_{10}H_{11}N_5O$<br>**MW:** 217.2 g/mol<br>**SMILES:** O=C1NN=C(C)CN1N=Cc2cccnc2 |  | 835.4100 Aerobic soil metabolism | 49921301<br><br>49921303 | PRT | | PRT |
| **MAJOR (>10%) TRANSFORMATION PRODUCTS** | | | | | | | |
| **CGA 359009 (CSAA441607, Metabolite D, M4, MB1, Metabolite 2U)** | **IUPAC:** 4,5-Dihydro-5-hydroxy-6-methyl-4-[(3-pyridinylmethylene)amino]-1,2,4-triazine-3-(2H)-one<br><br>**Formula:** $C_{10}H_{11}N_5O_2$<br>**MW:** 233.2 g/mol<br>**SMILES:** CC1=NNC(=O)N(\N=C\c2cccnc2)C1O |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | **14.3%** (5 d) | 0.1% (120 d) |
| | | | | 49921303 | Silt loam | **55.01%** (14 d) | 6.43% (363 d) |
| | | | | | Sandy loam | **44.97%** (3 d) | 1.57% (363 d) |
| **CGA 300407 (M3, MB10)** | **IUPAC:** 3-Pyridinecarboxaldehyde<br><br>**Formula:** $C_6H_5NO$<br>**MW:** 107.1 g/mol<br>**SMILES:** O=Cc1cccnc1 |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | **14.8%** (2 d) | ND (120 d) |
| | | | | 49921303 | Silt loam | 2.47% (363 d) | 2.47% (363 d) |
| | | | | | Sandy loam | 2.59% (90 d) | 1.99% (363 d) |

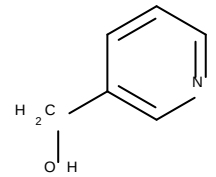
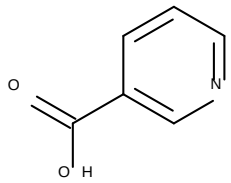
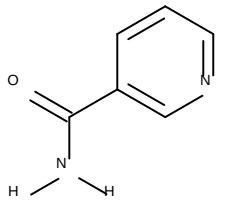
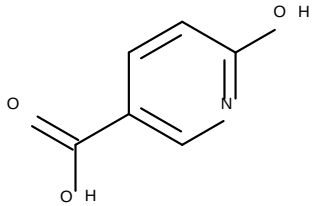
| Code Name/ Synonym | Chemical Name | Chemical Structure | Study Type | MRID | Maximum %AR (day) | | Final %AR (study length) |
|---|---|---|---|---|---|---|---|
| **CGA 363431 (MB5)** | **IUPAC:** 5-Hydroxy-6-methyl-4-[(6-oxo-l,6-dihydro-pyridine-3-ylmethylene)-amino]-4,5-dihydro-2H-[l,2,4]triazine-3-one<br><br>**Formula:** $C_{10}H_{11}N_5O_3$<br>**MW:** 249.2 g/mol<br>**SMILES:** CC1=NNC(=O)N(\N=C\C2=CNC(=O)C=C2)C1O |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | **15.6%** (10 d) | 0.9% (120 d) |
| | | | | 49921303 | Silt loam | **21.38%** (90 d) | **12.93%** (363 d) |
| | | | | | Sandy loam | **22.93%** (30 d) | 2.54% (363 d) |
| **CGA 255548** | **IUPAC:** 6-Hydroxypyridine-3-carbaldehyde<br><br>**Formula:** $C_6H_5NO_2$<br>**MW:** 123.1 g/mol<br>**SMILES:** Oc1ccc(C=O)cn1 |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | **16.2%** (24 d) | 1.1% (120 d) |
| **Carbon dioxide** | **IUPAC:** Carbon dioxide<br><br>**Formula:** $CO_2$<br>**MW:** 44 g/mol<br>**SMILES:** C(=O)=O |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | **73.1%** (120 d) | **73.1%** (120 d) |
| | | | | 49921303 | Silt loam | **22.48%** (363 d) | **22.48%** (363 d) |
| | | | | | Sandy loam | **30.55%** (363 d) | **30.55%** (363 d) |
| **Unextractable residues** | NA | NA | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | **52.9%** (80 d) | **49.1%** (120 d) |
| | | | | 49921303 | Silt loam | **42.22%** (272 d) | **41.86%** (363 d) |
| | | | | | Sandy loam | **65.95%** (150 d) | **47.37%** (363 d) |
| **MINOR (<10%) TRANSFORMATION PRODUCTS** | | | | | | | |

| Code Name/ Synonym | Chemical Name | Chemical Structure | Study Type | MRID | Maximum %AR (day) | | Final %AR (study length) |
|---|---|---|---|---|---|---|---|
| **CGA 371075 (CSAA447511, Metabolite C)** | **IUPAC:** 4,6-Dimethyl-2H-1,2,4-triazine-3,5-dione<br><br>**Formula:** $C_5H_7N_3O_2$<br>**MW:** 141.1 g/mol<br>**SMILES:**<br>CN1C(=O)NN=C(C)C1=O |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | 9.2% (50 d) | 6.4% (120 d) |
| **CGA 294849 (CSAA377032, Metabolite B)** | **IUPAC:** 4-Amino-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione<br><br>**Formula:** $C_4H_6N_4O_2$<br>**MW:** 142.1 g/mol<br>**SMILES:**<br>CC1=NNC(=O)N(N)C1=O |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | 8.8% (15 d) | 3.9% (120 d) |
| **CGA 363430 (MB4)** | **IUPAC:** 6-Methyl-4-[(6-oxo-l,6-dihydro-pyridine-3-ylmethylene)-ammo]-2H-[l,2,4]triazine-3,5-dione<br><br>**Formula:** $C_{10}H_9N_5O_3$<br>**MW:** 247.2 g/mol<br>**SMILES:**<br>CC1=NNC(=O)N(\N=C\C2=CNC(=O)C=C2)C1=O |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | 4.1% (10 d) | 0.6% (120 d) |
| | | | | 49921303 | Silt loam | 9.43% (150 d) | 8.36% (363 d) |
| | | | | | Sandy loam | 7.14% (59 d) | 3.03% (363 d) |
| **CGA 323584** | **IUPAC:** 6-Methyl-4-[(E)-3-pyridylmethyleneamino]-2H-1,2,4-triazine-3,5-dione<br><br>**Formula:** $C_{10}H_9N_5O_2$<br>**MW:** 231.2 g/mol<br>**SMILES:**<br>CC1=NNC(=O)N(\N=C\c2cccnc2)C1=O |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | 3.6% (1 d) | ND (120 d) |

| Code Name/ Synonym | Chemical Name | Chemical Structure | Study Type | MRID | Maximum %AR (day) | | Final %AR (study length) |
|---|---|---|---|---|---|---|---|
| **CGA 215525** | **IUPAC:** 4-Amino-6-methyl-2,5-dihydro-1,2,4-triazin-3-one<br><br>**Formula:** $C_4H_8N_4O$<br>**MW:** 128.1 g/mol<br>**SMILES:** CC1=NNC(=O)N(N)C1 |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | 3.1% (2 d) | ND (120 d) |
| **GS 23199 (CGA 324284)** | **IUPAC:** 6-Methyl-2H-1,2,4-triazine-3,5-dione<br><br>**Formula:** $C_4H_5N_3O_2$<br>**MW:** 127.1 g/mol<br>**SMILES:** CC1=NNC(=O)NC1=O |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | 1.4% (120 d) | 1.4% (120 d) |
| **SYN 510306** | **IUPAC:** 6-Methyl-4-[(E)-(6-oxo-1H-pyridin-3-yl)methyleneamino]-2,5-dihydro-1,2,4-triazin-3-one<br><br>**Formula:** $C_{10}H_{11}N_5O_2$<br>**MW:** 233.2 g/mol<br>**SMILES:** CC1=NNC(=O)N(C1)\N=C\C2=CNC(=O)C=C2 |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | 6.3% (10 d) | 0.1% (120 d) |
| **SYN 505866 (Unknown AE-4)[1]** | **IUPAC:** 4-Amino-5-hydroxy-6-methyl-2,5-dihydro-1,2,4-triazin-3-one<br><br>**Formula:** $C_4H_8N_4O_2$<br>**MW:** 144.1 g/mol<br>**SMILES:** CC1=NNC(=O)N(N)C1O |  | 835.4100 Aerobic soil metabolism | 49921301 | Sandy clay loam | 8.8% (15 d) | ND (120 d) |
| **REFERENCE COMPOUNDS NOT IDENTIFIED** | | | | | | | |

| Code Name/ Synonym | Chemical Name | Chemical Structure | Study Type | MRID | Maximum %AR (day) | Final %AR (study length) |
|---|---|---|---|---|---|---|
| **CGA 249257** | **IUPAC:** 6-Methyl-4,5-dihydro-2H-1,2,4-triazin-3-one<br><br>**Formula:** $C_4H_7N_3O$<br>**MW:** 113.1 g/mol<br>**SMILES:** CC1=NNC(=O)NC1 |  | 835.4100 Aerobic soil metabolism | 49921301 | NA | NA |
| **CGA 259168** | **IUPAC:** N-(6-methyl-3-oxo-2,5-dihydro-1,2,4-triazin-4-yl)acetamide<br><br>**Formula:** $C_6H_{10}N_4O_2$<br>**MW:** 170.2 g/mol<br>**SMILES:** CC(=O)NN1CC(=NNC1=O)C |  | 835.4100 Aerobic soil metabolism | 49921301 | NA | NA |
| **CGA 129539** | **IUPAC:** 2-(Pyridine-3-carbonylamino)acetic acid<br><br>**Formula:** $C_8H_8N_2O_3$<br>**MW:** 180.16 g/mol<br>**SMILES:** OC(=O)CNC(=O)c1cccnc1 |  | 835.4100 Aerobic soil metabolism | 49921303 | NA | NA |
| **CGA 245342** | **IUPAC:** 6-Methyl-4-[(E)-(1-oxidopyridin-1-ium-3-yl)methyleneamino]-2,5-dihydro-1,2,4-triazin-3-one<br><br>**Formula:** $C_{10}H_{11}N_5O_2$<br>**MW:** 233.2 g/mol<br>**SMILES:** CC1=NNC(=O)N(C1)\N=C\c2ccc[n+]([O-])c2 |  | 835.4100 Aerobic soil metabolism | 49921303 | NA | NA |

| Code Name/ Synonym | Chemical Name | Chemical Structure | Study Type | MRID | Maximum %AR (day) | Final %AR (study length) |
|---|---|---|---|---|---|---|
| **CGA 79452** | **IUPAC:** Pyridine-3-carbohydrazide<br><br>**Formula:** $C_6H_7N_3O$<br>**MW:** 137.13 g/mol<br>**SMILES:** NNC(=O)c1cccnc1 |  | 835.4100 Aerobic soil metabolism | 49921303 | NA | NA |
| **CGA 313124** | **IUPAC:** 6-(Hydroxymethyl)-4-[(E)-3-pyridylmethyleneamino]-2,5-dihydro-1,2,4-triazin-3-one<br><br>**Formula:** $C_{10}H_{11}N_5O_2$<br>**MW:** 233.2 g/mol<br>**SMILES:** OCC1=NNC(=O)N(C1)\N=C\c2cccnc2 |  | 835.4100 Aerobic soil metabolism | 49921303 | NA | NA |
| **CGA 96956** | **IUPAC:** 1-Methylpyridin-1-ium-3-carboxylate<br><br>**Formula:** $C_7H_7NO_2$<br>**MW:** 137.13 g/mol<br>**SMILES:** C[n+]1cccc(c1)C(=O)[O-] |  | 835.4100 Aerobic soil metabolism | 49921303 | NA | NA |
| **CGA 320484** | **IUPAC:** 4-[(E)-3-pyridylmethyleneamino]-2,5-dihydro-1,2,4-triazin-3-one<br><br>**Formula:** $C_9H_9N_5O$<br>**MW:** 203.2 g/mol<br>**SMILES:** O=C1NN=CCN1\N=C\c2cccnc2 |  | 835.4100 Aerobic soil metabolism | 49921303 | NA | NA |

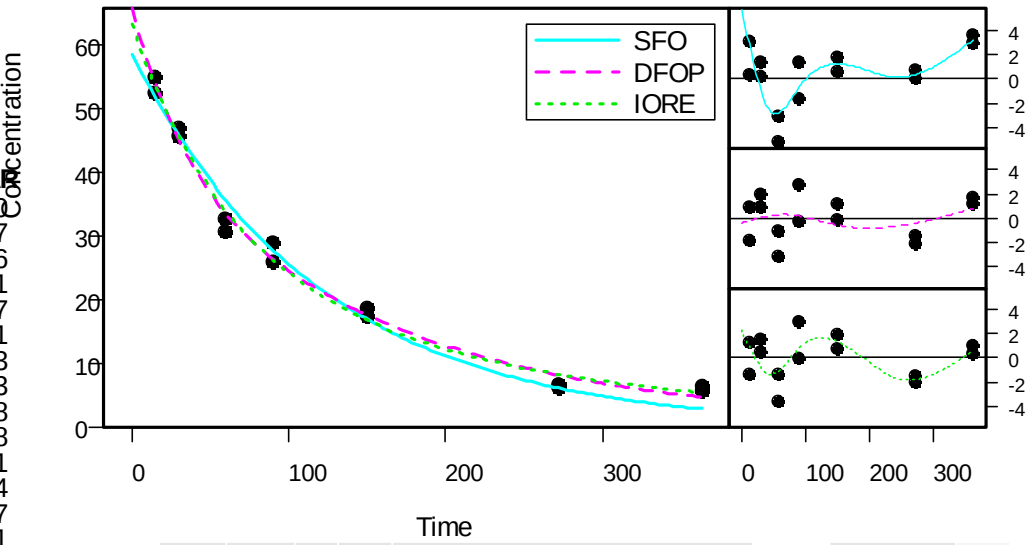
| Code Name/ Synonym | Chemical Name | Chemical Structure | Study Type | MRID | Maximum %AR (day) | Final %AR (study length) |
|---|---|---|---|---|---|---|
| **CGA 128632** | **IUPAC:** 3-Pyridylmethanol<br><br>**Formula:** $C_6H_7NO$<br>**MW:** 109.1 g/mol<br>**SMILES:** OCc1cccnc1 |  | 835.4100 Aerobic soil metabolism | 49921301<br>49921303 | NA | NA |
| **CGA 180777** | **IUPAC:** Nicotinic acid<br><br>**Formula:** $C_6H_5NO_2$<br>**MW:** 123.1 g/mol<br>**SMILES:** OC(=O)c1cccnc1 |  | 835.4100 Aerobic soil metabolism | 49921303 | NA | NA |
| **CGA 180778** | **IUPAC:** Pyridine-3-carboxamide<br><br>**Formula:** $C_6H_6N_2O$<br>**MW:** 122.1 g/mol<br>**SMILES:** NC(=O)c1cccnc1 |  | 835.4100 Aerobic soil metabolism | 49921303 | NA | NA |
| **CGA 319251** | **IUPAC:** 6-Hydroxypyridine-3-carboxylic acid<br><br>**Formula:** $C_6H_5NO_3$<br>**MW:** 139.1 g/mol<br>**SMILES:** OC(=O)c1ccc(O)nc1 |  | 835.4100 Aerobic soil metabolism | 49921303 | NA | NA |

[A] AR means “applied radioactivity”. MW means “molecular weight”. PRT means “parent”. ND means “not detected”. NA means “not applicable”.

**Attachment 2: Statistics Spreadsheets and Graphs**

# MB1 in aerobic silt loam soil

| Da | %AR |
|---|---|
| 1 | 55.0 |
| 3 | 45.7 |
| 5 | 30.6 |
| 9 | 26.1 |
| 15 | 18.7 |
| 27 | 6.81 |
| 36 | 6.43 |
| 1 | 52.3 |
| 3 | 46.8 |
| 5 | 32.8 |
| 9 | 29.1 |
| 15 | 17.4 |
| 27 | 6.17 |
| 36 | 5.81 |

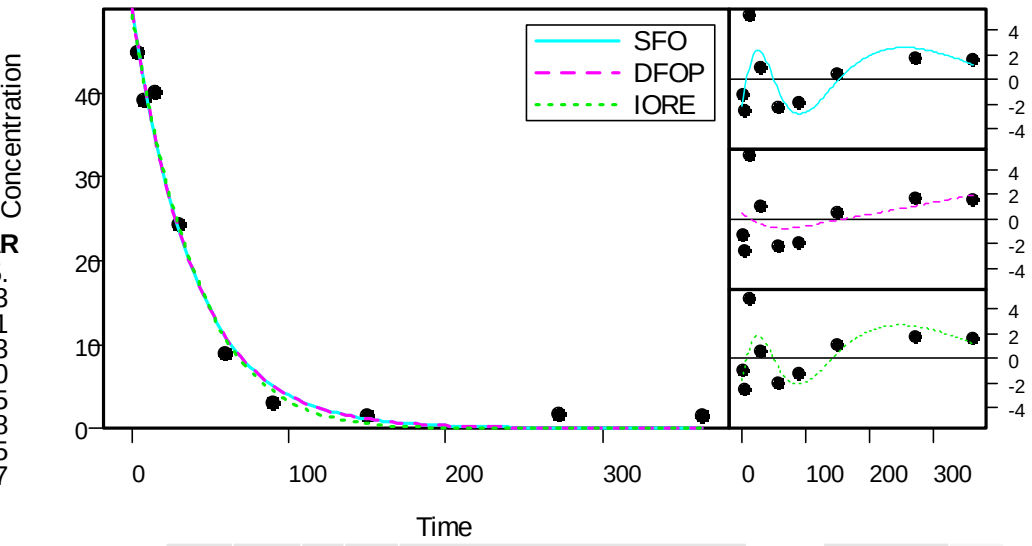



| | $DT_{50}$ | $DT_{90}$ | $\chi^2$ | $C_0$ | Parameters |
|---|---|---|---|---|---|
| SF | 83. | 27 | 6. | 58 | k 0.00827 |
| DF | 62. | 30 | 4. | 65 | f 0.337 $k_0$ 0.0312 $k_1$ 0.00612 |
| IOR | 68. | 33 | 4. | 63 | N 1.42 k 0.00205 |

| | |
|---|---|
| $S_C$ | 50.6 |
| $S_{SFO}$ | 77 |
| Slow $t_{1/2}$ | 113 |
| $t_{R IORE}$ | 99.2 |

# MB1 in aerobic sandy loam soil

| Da | %AR |
|---|---|
| 3 | 45. |
| 7 | 39.3 |
| 1 | 40.1 |
| 3 | 24.3 |
| 5 | 8.90 |
| 9 | 3.15 |
| 15 | 1.58 |
| 27 | 1.75 |
| 36 | 1.57 |



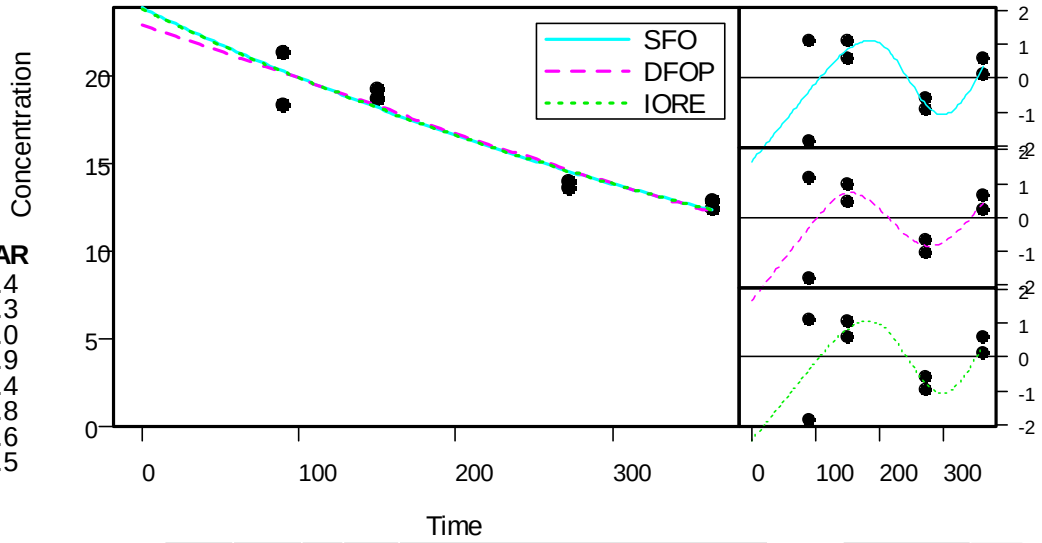

| | $DT_{50}$ | $DT_{90}$ | $\chi^2$ | $C_0$ | Parameters |
|---|---|---|---|---|---|
| SF | 27. | 90. | 1 | 5 | k 0.0254 |
| DF | 27. | 90. | 1 | 5 | f 0.785 $k_0$ 0.0254 $k_1$ 0.0254 |
| IOR | 28. | 86. | 1 | 49 | N 0.882 k 0.037 |

| | |
|---|---|
| $S_C$ | 62.6 |
| $S_{SFO}$ | 50 |
| Slow $t_{1/2}$ | 27.3 |
| $t_{R IORE}$ | 26 |

Kinetics models: Single First Order (SFO); Double First Order in Parallel (DFOP), and Indeterminate Order Rate Equation (IORE). Calculated half-lives and model parameters in accordance with the NAFTA kinetics guidance (USEPA, 2012).

# MB5 in aerobic silt loam soil

| Da | %AR |
|---|---|
| 9( | 21.4 |
| 15 | 19.3 |
| 27 | 14.0 |
| 36 | 12.9 |
| 9( | 18.4 |
| 15 | 18.8 |
| 27 | 13.6 |
| 36 | 12.5 |

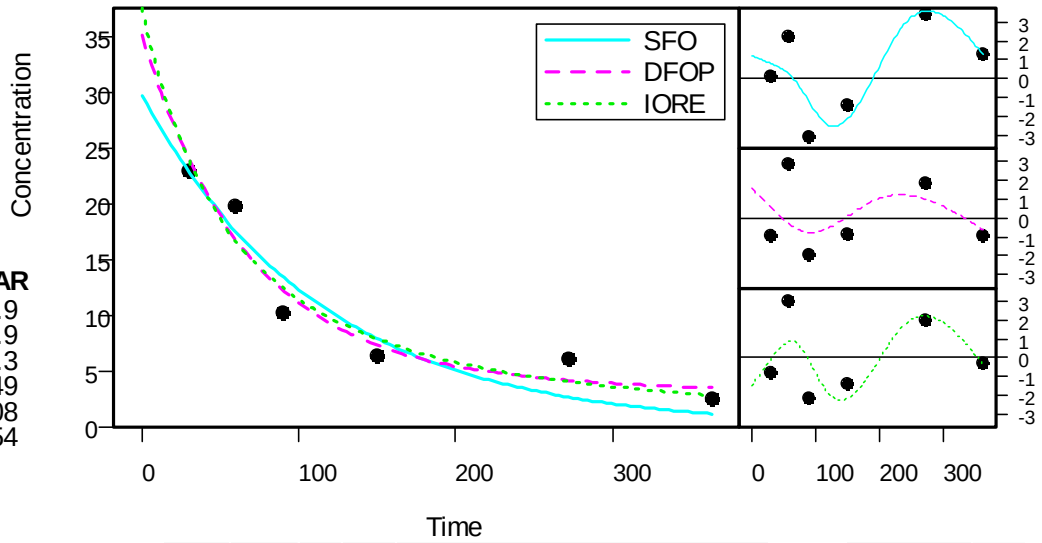



| | $DT_{50}$ | $DT_{90}$ | $\chi^2$ | $C_0$ | Parameters |
|---|---|---|---|---|---|
| SF( | 38 | 12[illegible] | 3. | 23 | k = 0.00181 |
| DF( | 39 | 11[illegible] | In | 2 | f = -0.325, $k_0$ = 0.0054, $k_1$ = 0.00228 |
| IOR | 38 | 12[illegible] | 3. | 23 | N = 0.949, k = 0.00209 |

| | |
|---|---|
| $S_C$ | 11.9 |
| $S_{SFO}$ | 7.71 |
| Slow $t_{1/2}$ | 305 |
| $t_{R=IORE}$ | 368 |

# MB5 in aerobic sandy loam soil

| Da | %AR |
|---|---|
| 3( | 22.9 |
| 5[illegible] | 19.9 |
| 9( | 10.3 |
| 15 | 6.49 |
| 27 | 6.08 |
| 36 | 2.54 |




| | $DT_{50}$ | $DT_{90}$ | $\chi^2$ | $C_0$ | Parameters |
|---|---|---|---|---|---|
| SF( | 78. | 26 | 1 | 29 | k = 0.00881 |
| DF( | 56. | 36 | 1 | 3 | f = 0.861, $k_0$ = 0.0151, $k_1$ = 0.000988 |
| IOR | 49. | 29 | 1 | 37 | N = 1.62, k = 0.00184 |

| | |
|---|---|
| $S_C$ | 41.4 |
| $S_{SFO}$ | 30.1 |
| Slow $t_{1/2}$ | 702 |
| $t_{R=IORE}$ | 88.2 |

Kinetics models: Single First Order (SFO); Double First Order in Parallel (DFOP), and Indeterminate Order Rate Equation (IORE). Calculated half-lives and model parameters in accordance with the NAFTA kinetics guidance (USEPA, 2012).

**DER Attachment 3: Calculations**

Calculations were performed by the reviewer using PestDF, and the following equations.

**Single First-Order (SFO) Model**

$$C_t = C_0 e^{-kt} \quad \text{(eq. 1)}$$

where,

$C_t$ = concentration at time t (%)
$C_0$ = initial concentration (%)
e = Euler's number (-)
k = SFO rate constant of decline ($d^{-1}$)
t = time (d)

The SFO equation is solved with PestDF by adjusting $C_0$ and $k$ to minimize the objective function ($S_{SFO}$) shown in equation 9.

$DT_{50}$ = natural log (2)/k (eq. 2)

$DT_{90}$ = ln (10)/k (eq. 3)

**Indeterminate Order Rate Equation (IORE) Model**

$$C_t = \left[C_0^{(1-N)} - (1-N)k_{IORE}t\right]^{\left(\frac{1}{1-N}\right)} \quad \text{(eq. 4)}$$

where,

N = order of decline rate (-)
$k_{IORE}$ = IORE rate constant of decline ($d^{-1}$)

This equation is solved with PestDF by adjusting $C_0$, $k_{IORE}$, and N to minimize the objective function for IORE (SIORE) (See equation 9). Half-lives for the IORE model are calculated using equation 5, which represents a first-order half-life that passes through the $DT_{90}$ of the IORE model. (Traditional $DT_{50}$ and $DT_{90}$ values for the IORE model can be calculated using equations 6 and 7.)

$$t_{IORE} = \frac{\log(2)}{\log(10)} \frac{{C_0}^{1-N}\left(1-0.1^{(1-N)}\right)}{(1-N)k_{IORE}} \quad \text{(eq. 5)}$$

$$DT_{50} = \frac{(C_0/2)^{(1-N)} - C_0^{(1-N)}}{k(N-1)} \quad \text{(eq. 6)}$$

$$DT_{90} = \frac{(C_0/10)^{(1-N)} - C_0^{(1-N)}}{k(N-1)} \quad \text{(eq. 7)}$$

**Double First-Order in Parallel (DFOP) Model**

$$C_t = C_0 g^{-k_1 t} + C_0(1-g)^{-k_1 t} \quad \text{(eq. 8)}$$

where,

g = the fraction of $C_0$ applied to compartment 1 (-)
$k_1$ = rate constant for compartment 1 ($d^{-1}$)
$k_2$ = rate constant for compartment 2 ($d^{-1}$)

If $C_0 \times g$ is set equal to *a* and $C_0(1-g)$ is set equal to *c*, then the equation can be solved with R kinetics software for *a*, *c*, $k_1$, and $k_2$ by minimizing the objective function ($S_{DFOP}$) as described in equation 9.

$DT_{50}$ and $DT_{90}$ values can be calculated using equations 2 and 3, with $k_1$ or $k_2$ in place of k.

Objective Function: SFO, IORE, and DFOP are solved by minimizing the objective function ($S_{SFO}$, $S_{IORE}$, or $S_{DFOP}$).

$$S_{SFO}, S_{IORE}, \text{ or } S_{DFOP} = \sum (C_{model,t} - C_{d,t})^2 \quad \text{(eq. 9)}$$

where,

$S_{SFO}$ , $S_{IORE}$, or $S_{DFOP}$ = objective function of kinetics model fit ($\%^2$)
n = number of data points (-)
$C_{model,t}$ = modeled value at time corresponding to $C_{d,t}$ (%)
$C_{d,t}$ = experimental concentration at time t (%)

**Critical Value to Determine Whether SFO is an Adequate Kinetics Model**

If $S_{SFO}$ is less than $S_C$, the SFO model is adequate to describe kinetics. If not, the faster of $t_{IORE}$ or the DFOP $DT_{50}$ for compartment 2 should be used.

$$S_c = S_{IORE}\left(1 + \frac{p}{n-p} F(\alpha, p, n-p)\right) \quad \text{(eq. 10)}$$

where,

$S_c$ = the critical value that defines the confidence contours ($\%^2$)
p = number of parameters (3 in this case)
α = the confidence level (0.50 in this case)
F(α, p, n-p) = F distribution with α level of confidence and degrees of freedom p and n-p